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# Polarized Infrared Spectra of Benzene Derivatives*

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The polarized infrared spectra of highly oriented crystals of *m*-dinitrobenzene, acetanilide and *p*-dimethoxybenzene were measured. The directions of transition moments of hydrogen out-of-plane vibrations and their combination bands were calculated from dichroic ratios, and were compared with the results of X-ray analysis.

The agreement was satisfactory in the case of *m*-dinitrobenzene which has an approximate $C_{2v}$ symmetry. For acetanilide, some differences were found between the infrared results and those of X-ray analysis when its benzene ring was assumed to have $C_{2v}$ symmetry. However, when $C_s$ symmetry was assumed, a good agreement was obtained.

## INTRODUCTION

It is well known that the frequencies of hydrogen out-of-plane vibrations of a benzene ring are determined almost entirely by the positions rather than the nature of substituents[1,2], and the combination bands (containing overtone) of these vibrations occur in the same general region as the characteristic bands of various types of aromatic substitution. The several bands appeared in the region 2000~1600 $cm^{-1}$ were assigned by Kakiuchi[3] who calculated the frequenceis and the relative intensities of the combinations.

The directions of transition moments of out-of-plane vibrations of benzene derivatives are perpendicular to the plane of the benzene ring, and those of the binary combinations of these vibrations are parallel to the plane. If the directions of transition moments of these bands are determined, the crystal structure may be presumed. In this paper, the directions of transition moments of several bands of hydrogen out-of-plane vibrations and their combinations were determined from dichroic ratios of these bands, and were compared with the results of X-ray analysis, with the aim of establishing a way to find the crystal structures of benzene derivatives by using the polarized light.

## THEORY

Bhagavantam and Venkatarayudu[4] have investigated the modes of vibrations of whole crystals by means of group theory. Ambrose, Elliott and Temple[5] have showed a way to determine the direction of the transition

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moment when the coupling between molecules within the unit cell is small.

In the case of orthorhombic crystals, if $D_j$, $D_k$ and $D_1$ are optical densities with the $E$ vector along $j$, $k$ and $1$ crystal axes respectively, the angle ($\theta_k^j$) between the projection of transition moment to $jk$ plane and $k$ axis can be expressed as follows:

$$\theta_k^j = \tan^{-1}(D_j/D_k)^{1/2} = \tan^{-1}(D_k^j)^{1/2} \qquad (1)$$

This relation can be used only when the coupling between molecules within the unit cell is small and no accidental degeneracy exists.

In this case, there are two possible directions, T.M.1 and T.M.2 as shown in Fig. 1, for the projection which makes an angle $\theta_k^j$ to $k$ axis. We can not tell at once which is the genuine direction. This is also true for $\theta_l^k$ and $\theta_l^j$. While, one of the $\theta_k^j$, $\theta_l^k$ and $\theta_l^j$ is determined as a function of the others by the following relation*.

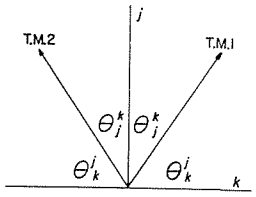


Fig. 1.

$$\tan\theta_k^j \times \tan\theta_l^k = \tan\theta_l^j \qquad (2)$$

Thererore, the four possible directions of transition moments must be considered for a pair of dichroic ratios of a given band.

It is necessary to refer to the molecular symmetry for the determination of the genuine direction out of the four directions. In the case of planar molecules, since the directions of transition moments are either perpendicular or parallel to the molecular plane, it is appropriate to choose the nearest one to these directions out of the four directions. In the case of $C_{2v}$ symmetry, it is adequate to choose as the genuine direction the one which is the nearest to any one of the directions of 2-fold axis and the two normals of the two planes of symmetry. Then, in the case of benzene derivatives, the genuine directions of transition moments were chosen under the assumption that the symmetry of the benzene ring is $C_s$ or $C_{2v}$ etc.

## EXPERIMENTAL

The samples used were manufactured by the Tokyo Kasei Co., which were purified by the recrystallization. Well oriented crystal layers of samples were obtained by cooling from the melts between two optically flat plates of rock-salt. Fairly large areas of uniform orientation were produced by touching melted samples at the edge of one of the windows with the seed crystals. In

* For example, in the special case where $\theta_k^j$ is 90° and $\theta_l^k$ is 0°, $\theta_l^j$ can not be determined uniquely.

this case, the oriented crystals in which various kinds of the crystal plane are parallel to the surface of rock-salt were obtained, then, the Miller indices of the planes were determined by using a shimazu GX-2A X-ray diffractometer.

Infrared spectra were measured with a Perkin Elmer model 21 spectrometer equipped with a LiF prism and a Koken DS-301 spectrometer equipped with two NaCl prisms. The application of the radiation polarized either parallel or perpendicular to the elongation direction of crystals was attained by rotating the oriented sample by 90°.

## RESULTS AND DISCUSSION

### 1) *m*-Dinitrobenzene

The crystal structure of *m*-dinitrobezene recrystalized from the water-ethanol mixture has already been reported by Trotter[6]. Their infrared spectra were comfirmed to be identical with those of crystals obtained from the melts by the KBr disk method.

The polarized infrared spectra (combination region) of two kinds of samples, in which (100) and (010) crystal faces are parallel to the surface of rock-salt respectively, are shown in Fig. 2(a) and (b), where the full lines are the

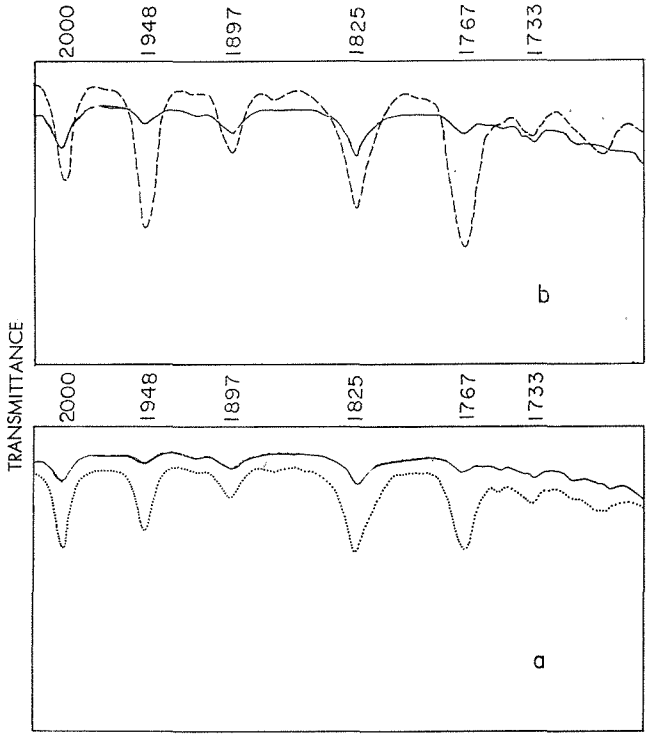


Fig. 2. Polarized infrared spectra of *m*-dinitrobenzene.
a : 100 section
——; *E* vector parallel to needle
·····; *E* vector perpendicular to needle
b : 010 section
——; *E* vector parallel to needle
– – –; *E* vector perpendicular to needle

absorption curves obtained with the polarized radiation having the $E$ vector parallel to the needle, and broken and dotted lines perpendicular.

Since full lines in (a) and (b) are the same, it it known that these are the spectra with the $E$ vector along the c crystal axis, and that the needle direction coincides with the c axis. Dotted and broken lines are, therefore, the spectra in which the $E$ vector is parallel to the b and a axes respectively.

The frequencies and the relative intensities of several bands in this region are shown in Table 1. These bands were assigned in accordance with Kakiuchi's results[3] under the assumption of $C_{2v}$ symmetry. The assignments are shown in the third column, where a, b, c and d represent the four out-of-plane

Table 1. Frequencies and assignments of the combinations of hydorogen out-of-plane vibrations of *m*-dinitrobenzene.

| Frequencies ($cm^{-1}$) | Intensities | Assignement | Species | Fundamental frequencies | Observed values |
|---|---|---|---|---|---|
| 2000 | s | 2 c | $A_1$ | c = 1000 | 996 |
| 1948 | s | c + d | $B_1$ | d = 984 | |
| — | | b + c | $A_1$ | | |
| 1897 | m | 2 d | $A_1$ | | |
| — | | b + d | $B_1$ | | |
| 1825 | s | 2 b | $A_1$ | b = 913 | 913 |
| — | | a + c | $A_1$ | | |
| 1767 | s | a + d | $B_1$ | a = 819 | 818 |
| 1733 | w | a + b | $A_1$ | | |
| — | | 2 a | $A_1$ | | |

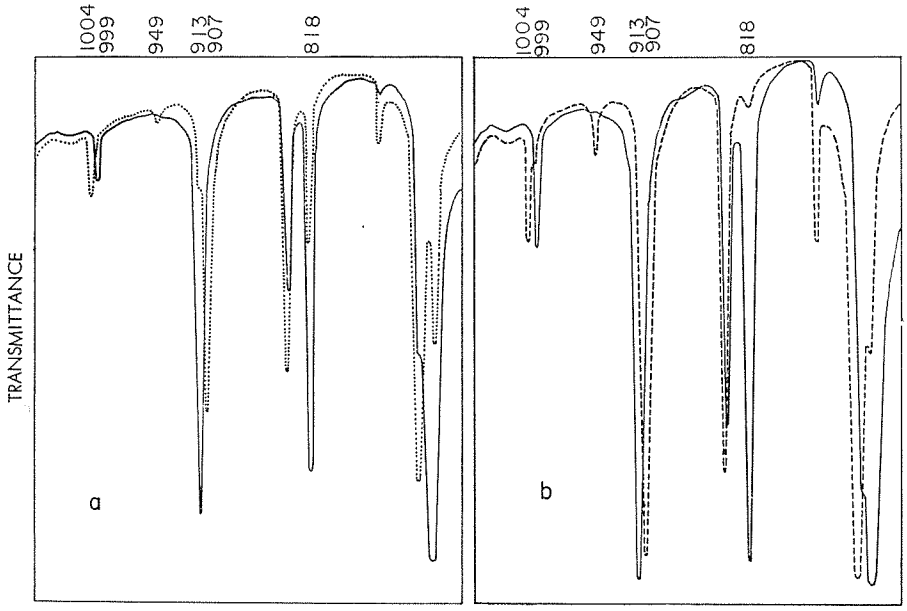


Fig. 3. Polarized infrared spectra of *m*-dinitrobenzene. Direction of $E$ vector as in Fig. 2.
a : 100 section, b : 010 section

fundamental vibrations of hydrogen atoms, 2a or 2b is the first overtone of a or b vibration etc., and a+b represents the combination of a and b etc. The four fundamental vibrations are divided into three infrared active ($B_2$) vibrations, namely a, b and c, and one infrared inactive ($A_2$) vibration d. The species of combinations, which are obtained as the direct product of the species of fundamentals, are shown in the fourth column. Fundamental frequencies and the assignments of combinations are shown in the fifth column.

The spectra in the region of fundamental out-of-plane vibrations of hydrogen atoms are shown in Fig. 3(a) and (b). The observed frequencies of fundamentals are shown in the sixth column, which agreed with the frequencies calculated from the combinations.

The selection rule shows that the directions of transition moments of the fundamental out-of-plane ($B_2$) vibration of benzene ring are parallel to the direction of the normal to the ring, and those of $A_1$ and $B_1$ vibrations of the combinations are parallel to the direction of the 2-fold axis and to the direction perpendicular to this axis in the plane of the ring, respectively. Therefore, from the results of X-ray analysis, $\theta_c^a$〔X〕* and $\theta_c^b$〔X〕 of these three directions are estimated and shown in Table 2. The carbon atom bonded to one of the nitro group is numbered $C_1$, and five other carbon atoms are numbered successively in such a manner that the carbon atom bonded to the other nitro group is $C_3$. The transition moments of $A_1$, $B_1$ and $B_2$ vibrations are assumed to have the directions of $C_2$–$C_5$, $C_4$–$C_6$ and the normal to the benzene ring, respectively.

Table 2. Angles calculated from X-ray analysis of *m*-dinitrobenzene.

| Species | $\theta_c^b$〔X〕 | $\theta_c^a$〔X〕 | Directions |
|---|---|---|---|
| $A_1$ | 63° | 56° | $C_2$–$C_5$ |
| $B_1$ | 75° | 80° | $C_4$–$C_6$ |
| $B_2$ | 24° | 5° | *normal to ring* |

Due to the imperfection of polarization in the transmitted beam of AgCl polarizer used, the apparent dichroic ratio differs from the true dichroic ratio. In order to obtain true dichroic ratios ($D_k^j$) from apparent values, the present author derived the following equation (see appendix):

$$D_k^j=\frac{\log[(1-t_m)/(T_j-t_mT_k)]}{\log[(1-t_m)/(T_k-t_mT_j)]} \tag{3}$$

where $t_m$ represents the imperfection of polarization of the transmitted beam, and $T_j$ and $T_k$ are observed transmittances when $j$ and $k$ crystal axes coincide with the $p$ direction respectively. If $I_p$ is the $p$-component of the intensity of polarized radiation, the perpendicular component ($I_t$) of the radiation is $t_mI_p$.

* 〔X〕 denotes the results of X-ray analysis.

The dichroic ratios of fundamentals and the combinations of out-of-plane vibrations of hydrogen atoms are shown in Table 3. The $\theta_c^b$ and $\theta_c^a$ calculated from the dichroic ratios are shown in the fourth and sixth columns. Comparison between these values and the results (Table 2) of the X-ray analysis shows that the agreements are satisfactory except for a band at 1897 $cm^{-1}$.

Table 3. Angles obtained from dichroic ratios of *m*-dinitrobenzene.

| Frequencies ($cm^{-1}$) | Species | $D_c^b$ | $\theta_c^b$ | $D_c^a$ | $\theta_c^a$ |
|---|---|---|---|---|---|
| 2000 | $A_1$ | 4.54 | 65° | 2.86 | 59° |
| 1948 | $B_1$ | 18.94 | 77° | 21.65 | 78° |
| 1897 | $A_1$ | 2.16 | 56° | 2.85 | 59° |
| 1825 | $A_1$ | 3.94 | 63° | 3.35 | 61° |
| 1767 | $B_1$ | 16.88 | 76° | 20.81 | 78° |
| 818 | $B_2$ | 0.26 | 27° | 0.01 | 6° |

The following reason may be considered for the differences of about 7° for the band at 1897 $cm^{-1}$. Since this band is assigned to 2d vibration, the frequency of d vibration must be about 949 $cm^{-1}$. In spite of the infrared inactive ($A_2$) vibration, there is a band at 949 $cm^{-1}$, which shows dichroisms of $B_1$ vibration (see Fig. 3). Combination of this $B_1$ vibration and the d vibration is an infrared active ($B_2$) vibration, which accidentally degenerates with a 2d vibration. Since combinations of the d vibration and other out-of-plane vibrations of hydrogen atoms are infrared inactive ($A_2$) vibrations, they do not affect the dichroic ratios of the combinations except for the band at 1897 $cm^{-1}$.

The dichroic ratios of two bands at 999 (c vibration) and 913 $cm^{-1}$ (b vibration) can not be calculated because the bands overlap with other bands (which may be assigned to the $B_1$ vibrations), but the spectra show the expected dichroisms.

### 2) Acetanilide

Abbott and Elliott[7] have measured the polarized infrared spectra of acetanilide in which (100) and (001) crystal planes are parallel to the surface of rock-salt, and calculated the directions of transition moments. They reported that the directions of transition moments of two bands at ca. 761 and ca. 905 $cm^{-1}$ are only a few degrees different from the direction of the normal to the plane of ring and no doubt the transitions are out-of-plane vibrations of hydrogen atoms. However, they did not refer to the combinations of out-of-plane vibrations of hydrogen atoms.

The polarized infrared spectra of thick samples were measured in the region of combinations of out-of-plane vibrations and were shown in Fig. 4(a) and (b). Similarly to Fig. 2, full, dotted and broken lines may be considered as the spectra with the $E$ vector along the b, c and a crystal axes respectively.

Frequencies and relative intensities in this region are shown in the first and the second columns of Table 4. The third column shows the assignments

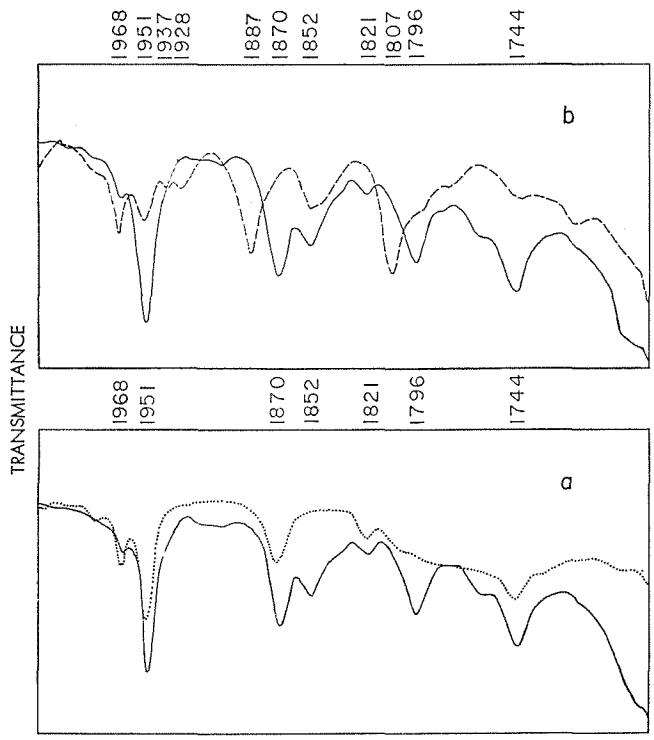


Fig. 4. Polarized infrared spectra of acetanilide. Direction of $E$ vector as in Fig. 2.
a : 100 section b : 001 section

Table 4. Frequencies and assignments of the combinations of hydrogen out-of-plane vibrations of actanilide.

| Frequencies ($cm^{-1}$) | Intensities | Assignments | Species | Fundamental frequencies | Observed values |
|---|---|---|---|---|---|
| 1968 | m | 2c | $A_1$ | c =983 | 986 |
| 1951 | s | c + e | $B_1$ | e =967 | |
| 1937 | w | 2e | $A_1$ | | |
| 1928 | w | | | | |
| 1887 | m | b + c | $A_1$ | b =903 | 905 |
| 1870 | m | b + e | $B_1$ | | |
| 1852 | m | * | | | |
| 1821 | w | c + d | $B_1$ | d =837 | |
| 1807 | m | d + e | $A_1$ | | |
| — | | 2b | $A_1$ | | |
| 1796 | m | * | | | |
| 1744 | w | b + d | $B_1$ | | |

of bands in this region, which are determined on the basis of Kakiuchi's results[3]. The five out-of-plane vibrations of hydrogen atoms are divided into three infrared active ($B_2$) vibrations, a, b and c, and two infrared inactive ($A_2$) vibrations, d and e.

The bands with the asterisk could not be identified with the combinations of out-of-plane vibrations of hydrogen atoms, and may be attributed to the amide group. The fourth column shows the species of the combinations, and the fifth column shows the fundamental frequencies calculated from the combinations, which agree satisfactorily with the observed values (seventh column).

From the X-ray analysis, $\theta_b^x$[X] and $\theta_c^x$[X] of $A_1$, $B_1$ and $B_2$ vibrations are estimated and are shown in Table 5, assuming that the directions of transition moments of $A_1$, $B_1$ and $B_2$ vibrations are parallel to those of $C_1$-$C_4$, $C_2$-$C_6$ and the normal to the ring respectively. Dichroic ratios, $\theta_b^x$ and $\theta_c^x$ are shown in Table 6. The agreement between the results of infrared study and those of X-ray analysis (Table 5) are not so good.

Table 5. Angles calculated from X-ray analysis of acetanilide.

| Species | $\theta_b^x$[X] | $\theta_c^x$[X] | Directions |
|---|---|---|---|
| $A_1$ | 81° | 22° | $C_1$-$C_4$ |
| $B_1$ | 20° | 59° | $C_2$-$C_6$ |
| $B_2$ | 21° | 34° | normal to ring |

Table 6. Angles obtained from dichroic ratios of acetanilide.

| Frequencies ($cm^{-1}$) | Species | $D_b^x$ | $\theta_b^x$ | $D_c^x$ | $\theta_c^x$ |
|---|---|---|---|---|---|
| 1968 | $A_1$ | 4.20 | 64° | 0.46 | 34° |
| 1951 | $B_1$ | 0.23 | 26° | 1.77 | 53° |
| 1887 | $A_1$ | | 90° | 0 | 0° |
| 1870 | $B_1$ | 0 | 0° | 2.47 | 58° |
| 1807 | $A_1$ | | 90° | 0 | 0° |
| 905 | $B_2$ | 0.33 | 30° | 0.23 | 25° |
| 761 | $B_2$ | 0.14 | 21° | 0.49 | 35° |

So far, the symmetry of the benzene ring has been assumed as $C_{2v}$. Then let us assume instead that it is $C_s$. From the results of X-ray analysis, the equation of the mean plane of the ring is evaluated to be[8]

$$x - 2.658y - 3.897z = 2.086$$

where x, y and z are coordinates (in Å unit) corresponding to a, b and c crystal axes respectively.

Angles between this plane and the directions of transition moments calculated from dichroic ratios are estimated to be small. Namely, it was shown that the transition moments of combinations of out-of-plane vibrations of hydrogen atoms are parallel to the plane of the ring. Fig. 5 shows the directions of transition moments of the combinations.

The directions of transition moments of the two bands at 1852 and 1796 $cm^{-1}$, which are marked with the asterisk in Table 4, are at an angle of about

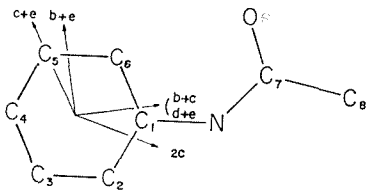


Fig. 5. Directions of transition moments for combinations of hydrogen out-of-plane vibrations of acetanilide.

25° to the plane of the ring, but lie in the plane of the amide group. Therefore, these bands are considered to be the combination bands of this group.

The dichroic ratios of out-of-plane (fundamental) vibrations of hydrogen atoms have been reported by Abbott etc.[7], which agreed well with the results obtained by the present author.

In the case of the a vibration, $\theta_c^b$ and $\theta_c^b[X]$ as well as $\theta_b^a$ and $\theta_b^a[X]$ have the same values, as shown in Tables 5 and 6, whereas those of the b vibration have different values. The direction of transition moment of the b vibration makes an angle of about 12° with that of the normal to the plane of the ring.

### 3) *p*-Dimethoxybenzene

Goodwin, Przybylska and Robertson[9] have given the crystal structure of *p*-dimethoxybenzene, in which the molecule has an approximate $C_{2h}$ symmetry.

It was found that the specimens usually crystallized with the (001) plane parallel to the surface of rock-salt, but it was difficult to make the sample with another face parallel to it.

Over the region of the combinations, two bands were found at 1866 and 1637 $cm^{-1}$ for the sample with the (001) plane parallel to the surface of rock-salt. If the symmetry of benzene ring is assumed $V_h$, these bands are assigned to b+d and a+b vibrations respectively ($B_{3u}$ vibrations both) in accordance with Kakiuchi's results. The two $B_{2u}$ vibrations, which are b+d and a+c vibrations, were expected to show stronger bands when the $E$ vector is parallel to the c axis. In fact, one band is observed at 1747 $cm^{-1}$ for the sample in which the (100) or (010) crystal face is parallel to the surface of rock-salt in considerable part. This band was identified to the b+d vibration by comparing with the results of *p*-dichlorobenzene[3]. The results are shown in Table 7.

Table 7. Frequencies and assignments of the combinations of hydrogen out-of-plane vibrations of *p*-dimethoxybenzene.

| Frequencies ($cm^{-1}$) | Intensities | Assignments | Species |
|---|---|---|---|
| 1866 | s | c + d | $B_{3u}$ |
| 1748 | w | b + d | $B_{2u}$ |
| — | | a + c | $B_{2u}$ |
| 1637 | s | a + b | $B_{3u}$ |

From the results of X-ray analysis[9], values of $\theta_b^a$〔X〕 of $B_{1u}$, $B_{2u}$ and $B_{3u}$ vibrations are calculated, and shown in Table 8, where the directions of transition moments of $B_{1u}$, $B_{2u}$ and $B_{3u}$ vibrations are taken to the direction of the normal to the ring, that connecting the two carbon atoms bonded to the methoxy groups, and that connecting the two carbon atoms adjacent to an atom bonded to one methoxy group, respectively.

Table 8. Angles calculated from X-ray analysis of *p*-dimethoxybenzene.

| Species | $\theta_b^a$〔X〕 | Directions |
|---|---|---|
| $B_{1u}$ | 59° | normal to ring |
| $B_{2u}$ | 5° | $C_1$-$C_1'$ |
| $B_{3u}$ | 37° | $C_2$-$C_3'$ |

Table 9. Angles obtained from dichroic ratios of *p*-dimethoxybenezene.

| Frequencies ($cm^{-1}$) | Species | $D_b^z$ | $\theta_b^z$ |
|---|---|---|---|
| 1866 | $B_{3u}$ | 0.90 | 43° |
| 1637 | $B_{3u}$ | 1.03 | 45° |
| 829 | $B_{1u}$ | 2.37 | 57° |

Table 9 shows the dichroic ratios and the $\theta_b^z$ calculated from these values. The $\theta_b^z$ of the band at 829 $cm^{-1}$ agreed with the $\theta_b^a$〔X〕 estimated from the results of X-ray analysis, which is assigned to the fundamental out-of-plane vibration of hydrogen atoms. While, the $\theta_b^z$ of the two $B_{3u}$ combinations are about 10° different from the expected value. Comparing with the results of acetanilide, it seems that a better agreement will be obtained if the symmetry is assumed $C_{2h}$ rather than $V_h$.

## CONCLUSION

In the case of *m*-dinitrobenzene, the directions of transition moments calculated from dichroic ratios of hydrogen out-of-plane vibrations and their combinations agreed with directions estimated from the results of X-ray analysis, except the band at 1897 $cm^{-1}$ which seems to have an accidental degeneracy. In the case of acetanilide in which $C_s$ symmetry is assumed, good agreements were also obtained. From these agseements, it is concluded that the interaction between molecules within the unit cell is negligible concerning the hydrogen out-of-plane vibrations and their combinations of benzene derivatives.

If the symmetry of the whole molecule is $V_h$ or $C_{2v}$ etc., the angles between crystal axes and the plane of benzene ring as well as the bonded direction may be presumed, by measuring dichroic ratios of hydrogen out-of-plane vibra-

tion and their combinations.

While, if the symmetry of the whole molecule is lowered, only angles between the crystal axes and the plane of the ring can be presumed, but we can not obtain the information about the bond direction. Considering the accidental degeneracy, it is desirable to use as many bands as possible for a further study of the crystal structures.

## APPENDIX

When measurements are made with the $E$ vector of the linearly polarized portion of the beam at 45° to the slit, and $E$ vector is parallel to $j$ and $k$ crystal axes respectively, dichroic ratios are given as follows:[10]

$$R_{\pm}=\frac{\ln[(1+t_m)/(\beta_j+t_m\beta_k)]}{\ln[(1+t_m)/(\beta_k+t_m\beta_j)]} \tag{4}$$

where the subscripts + and − are used to designate 45° orientations 90° apart, and $\beta_j$ and $\beta_k$ are transmittances when the $E$ vector of perfectly polarized portion of the beam are parallel to $j$ and $k$ crystal axes respectively. $R_{\pm}$ is the observed dichroic ratio. $\beta_j$ and $\beta_k$ can not be measured directly by using an imperfect polarizer.

If the lights polarized by the polarizer and monochrometer are detected, and the fractions of $p$- and $i$-components of the energy of the polarized light are $t_p$ and $t_i$, respectively, we have

$$t_p+t_i=1. \tag{5}$$

If the transmittances are $T_j$ and $T_k$ for the $p$-direction parallel to $j$ and $k$ axes respectively, they are given by

$$\frac{t_p\beta_j+t_i\beta_k}{t_p+t_i}=T_j \quad (p\|j) \tag{6}$$

$$\frac{t_p\beta_k+t_i\beta_j}{t_p+t_i}=T_k \quad (p\|k). \tag{7}$$

Equation (3) is obtained from equations (5), (6) and (7) together with the following equation which expresses the true dichroic ratio ($R_T$):

$$R_T=\frac{\ln(1/\beta_j)}{\ln(1/\beta_k)}. \tag{8}$$

From a similar consideration it is found that, if the bands due to one mode show different frequencies when the $E$ vector is parallel to each of the three crystal axes, the dichroic ratio is given by

$$D_k^j=\frac{\log[(1-t_m)/(T_j-t_mT_k)]_{\nu_j}}{\log[(1-t_m)/(T_k-t_mT_j)]_{\nu_k}}, \tag{9}$$

where $\nu_j$ and $\nu_k$ represent the frequencies with the $E$ vector along $j$ and $k$ axes respectively.

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